



# Preparation of TiO<sub>2</sub>-polystyrene photocatalyst from waste material and its usability for removal of various pollutants

İlknur Altın, Münevver Sökmen\*

Department of Chemistry, Faculty of Science, Karadeniz Technical University, 61080 Trabzon, Turkey



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## ABSTRACT

The present study has concentrated on the immobilization of anatase titanium dioxide particles (TiO<sub>2</sub>, 44 nm particle size) on polystyrene (PS) by thermal attachment process. Waste PS particles were used as a support material. The photocatalytic properties of the produced material were tested for degradative removal of methylene blue, reductive removal of Cr(VI) as model pollutants and its antimicrobial properties were investigated using *Escherichia coli* and *Aspergillus niger* as model microorganisms employing a near visible UV-A light (365 nm) source. Thus, TiO<sub>2</sub> immobilized polystyrene beads seem to be highly promising for successful removal of studied pollutants. Additionally, effect of various experimental parameters such as pH, pollutant concentrations and catalyst mass has been evaluated as much as its stability and reusability. Control experiments indicated that employing neat PS in the presence and absence of light does not provide significant removal under the same condition.

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## 1. Introduction

Water is one of the most essential requirements for the life on earth and indispensable to sustain the biological activities of organisms. It is under serious threat as a consequence of chemical and microbial contamination due to the population growth and the development of industry. Clean water, which is very important for the life, must be distributed to people after proper removal of all pollutants. Less developed and developing countries have faced special difficulties in meeting the demand for pure water by treatment.

Various methods are currently used for treatment of industrial contaminated waste water such as reverse osmosis, chemical precipitation, activated carbon adsorption, membrane filtration and ion exchange [1,2]. However, these techniques often transfer the pollutants from one phase to another and causing secondary pollution problems [3,4]. In fact most of these techniques require further treatment processes which are costly and often ineffective at low pollutant concentrations.

Considerable attention has been paid to heterogeneous photocatalytic systems which involve photocatalyst and ultraviolet or sunlight in aqueous medium as an efficient and eco-friendly technology for the removal of pollutants from water [5–8]. Among the various semiconductor materials, titanium dioxide (TiO<sub>2</sub>) has proved as the most suitable photocatalysis for widespread

environmental applications due to its harmless, low-cost, resistance to photocorrosion, biologically and chemically inert and high reactivity properties [9].

Heterogeneous photocatalytic removal of organic, inorganic and microbial contaminants has been discussed widely in the literature [10,11]. Briefly, when TiO<sub>2</sub> photocatalyst are illuminated by light of energy equal to or greater than its band gap (3.2 eV), produce electron–hole pairs, holes in the valence band (h<sup>+</sup> vb) and electrons in the conduction bands (e<sup>−</sup> cb). Some of the charge migrates to the photocatalyst's surface and reacts with the adsorbed species resulting in redox reactions. Valence band holes react with water or hydroxide ions to produce hydroxyl radicals (HO•), while the adsorbed oxygen molecule reacts with photo-generated electrons to generate active superoxide radical (O<sub>2</sub>•<sup>−</sup>) which, in turn, transforms into highly reactive species such as HO•, HO<sub>2</sub>• and H<sub>2</sub>O<sub>2</sub> [12,13]. These active radical species play an important role in the degradation of organic pollutants and disinfection of pathogenic microorganisms, while excited electrons are crucial to the photocatalytic reduction of toxic heavy metal ions.

Photoactive TiO<sub>2</sub> particles can be utilized both in the form of suspension and immobilized form on a surface. However, due to the sophisticated filtration of the suspended photoactive nanoparticles from the reaction medium after treatment period, its practical and economical application appear to be so difficult [14,15]. Immobilization of TiO<sub>2</sub> on a surface is an effective route to overcome disadvantages. But it usually reduces photocatalytic activity because of the distance between the particle and the species to be degraded. Consequently, this interaction (physical and/or chemical) should be checked for TiO<sub>2</sub> immobilized on the material surface

\* Corresponding author. Tel.: +90 462 377 25 32; fax: +90 462 325 31 96.  
E-mail address: [msokmen@ktu.edu.tr](mailto:msokmen@ktu.edu.tr) (M. Sökmen).

whether the produced material have a good separation performance or not. Different immobilization techniques and support materials are used to produce these types of materials. Polymeric materials are especially preferred due to their ease of production and low cost of which polystyrene (PS) is one of the best materials because of its inert nature and buoyant properties.

There are some published studies involving the preparation and photocatalytic properties of TiO<sub>2</sub> immobilized polystyrene (TiO<sub>2</sub>-PS) [16–24]. In one study Fa et al. [21] have investigated the solid-phase photocatalytic degradation of PS films by embedding the iron phthalocyanine immobilized TiO<sub>2</sub> nanoparticles into the commercial PS.

In another study PS had been used as template for production of porous TiO<sub>2</sub> nanoparticles [16,17]. Some researchers had investigated immobilization of TiO<sub>2</sub> nanoparticles onto PS to degrade waste PS itself [18–21] while TiO<sub>2</sub>-PS was also used to degrade methylene blue (MB) [22–24] as model pollutant.

Fabiyyi and Skelton [22] have developed a simple method for immobilization of TiO<sub>2</sub> nanoparticles on PS beads using a thermal attachment method. Degradation rates were 0.15–0.25  $\mu\text{mol min}^{-1}$  depending on catalyst mass between 0.5 and 7 g catalyst mass. Magalhães and Lago [24] have reported the preparation of TiO<sub>2</sub> immobilized on expanded polystyrene (TiO<sub>2</sub>/EPS) by grafting TiO<sub>2</sub> particles on the EPS surface. The photocatalytic studies were carried out with 50 mg L<sup>-1</sup> MB for 300 min irradiation (254 nm Hg lamp) which has resulted in approximately 60% discoloration of the dye.

In the present study, a thermal attachment procedure was employed for the anchoring anatase TiO<sub>2</sub> nanoparticles (44 nm particle size) on PS beads. PS material employed for immobilization was a waste material which was obtained during the production and fabrication of PS insulation material. These dusty small PS particles are great concern by the producers and should be utilized, destroyed or damped in some way. So, there is need for the development of proper and economical immobilization method (producing buoyant PS particles with photocatalytic properties) for employment into various applications. The aim of the study was to investigate the photocatalytic activity of the produced material for degradative removal of the organic or inorganic model pollutants such as methylene blue and highly toxic Cr(VI), and to assess its antimicrobial properties for *Escherichia coli* and *Aspergillus niger* as model microorganisms. MB removal studies which include pH, initial concentration and catalyst mass were investigated and interpreted in terms of various analytical variables. Photocatalytic reduction studies have been carried out in the presence of hole scavengers such as ethylenediaminetetraacetic acid (EDTA), oxalic acid and methanol to enhance photocatalytic reduction of Cr(VI) to Cr(III) [25–29]. TiO<sub>2</sub>-PS might be an important composite material with antimicrobial properties. *E. coli* has been used as model bacterial source in order to evaluate the antibacterial efficiency of TiO<sub>2</sub>-PS. On the other hand *A. niger* is a fungus especially grown in humid environments that should also be removed from water and in this regard polystyrene waste can be employed to remove or degrade the pollutant present in various environments. PS is an inert plastic and is non-biodegradable in the natural environment. The waste PS material produced during the production of insulation materials do not decompose in landfills. A large amount of disposable PS by-products cause serious environmental problems, called “white pollution”. In this manner, polystyrene waste, cannot be recycled, can be employed to remove or degradation another pollutants present in various environments such as water and air. Thus, aims to contribute to the economy. If the produced material proves highly effective for the above mentioned pollutants it will have important applications as industrial material for water remediation systems or for the construction industry. Reusability of the prepared material

was also determined since it is crucial for its industrial applications.

## 2. Experimental

### 2.1. Immobilization of TiO<sub>2</sub> on polystyrene (TiO<sub>2</sub>-PS)

PS particles (supplied by Politek, Trabzon/Turkey) used for immobilization were in different size between 500 and 800  $\mu\text{m}$  diameter round beads. If necessary a sieving process was applied before immobilization process. A thermal attachment procedure was employed for the anchoring TiO<sub>2</sub> nanoparticles (Sigma–Aldrich) on the polystyrene beads [22]. The attachment of the particles required mixing nearly 10:1 mass ratio of TiO<sub>2</sub> anatase to polystyrene in a crucible, and mixing thoroughly. The mixture was then placed in an oven and a temperature programme was applied. The oven temperature was initially at room temperature then was set at 162 °C at 20 °C min<sup>-1</sup>. As the temperature gradually increases to glass transition point of expanded polystyrene beads (approx. 150 °C) their surface softens so TiO<sub>2</sub> nanoparticles adhere to the soft surface of the PS. The crucible containing polystyrene or TiO<sub>2</sub> immobilized polystyrene was taken out and cooled down to room temperature in a desiccator. TiO<sub>2</sub> nanoparticles were separated from TiO<sub>2</sub>-PS materials by employing a 100  $\mu\text{m}$  sieve. Hereby, this method does not require the usage of some expensive chemicals and high energy so the immobilization method is very economical and practical.

### 2.2. Structural and surface analysis

The produced TiO<sub>2</sub>-PS were characterized by scanning-electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis, X-ray diffraction (XRD) and binocular microscopy. Surface characterization and deformation before and after light exposure should be carried out. The X-ray diffraction (XRD) data of the material was taken using a Rigaku D/Max-IIIC diffractometer with CuK $\alpha$  radiation over the range  $2\theta=20\text{--}60^\circ$  at room temperature. The surface morphology of the prepared material was analyzed using a JEOL JST-6400 scanning electron microscope combined with energy dispersive X-ray (EDX) analysis at 15 kV voltage. Binocular microscope was used for testing durability of PS or TiO<sub>2</sub>-PS. Thermogravimetric analysis and Fourier transform infrared spectroscopy (FT-IR, PerkinElmer 1600 FT-IR spectrophotometer, 4000–450 cm<sup>-1</sup>) analysis were also performed before and after exposure. A Seiko II Exstar 6000 thermal analyzer was used to record DTA curves under nitrogen atmosphere with a heating rate of 20 °C min<sup>-1</sup> in the temperature range 30–700 °C using platinum crucibles.

### 2.3. Photocatalytic activity of TiO<sub>2</sub>-PS

Initially, durability tests of the TiO<sub>2</sub>-PS were carried out in the presence of acidic, neutral or basic solutions (pH 2, 7 or 10) and organic solution (ethanol) for 24 h. Analytical grade chemicals and solvents were used for all experiments mainly purchased from Merck. Thus, microscope image of neat or TiO<sub>2</sub>-PS has been taken before and after the treatment in order to test their resistance to environmental conditions.

Photocatalytic efficiencies were tested for the removal of aqueous solution of methylene blue (MB) or Cr(VI) ions in the presence and absence of light, PS and TiO<sub>2</sub>-PS. A set of experiments were designed to compare the photocatalytic actions of the TiO<sub>2</sub>-PS materials with PS. Surface or structural variation studies of neat PS and TiO<sub>2</sub>-PS were carried out in water with a UV-A emitting lamp (365 nm, Spectroline ENF-260). The effects of analytical parameters, that is, pH, MB concentration, catalyst mass on the

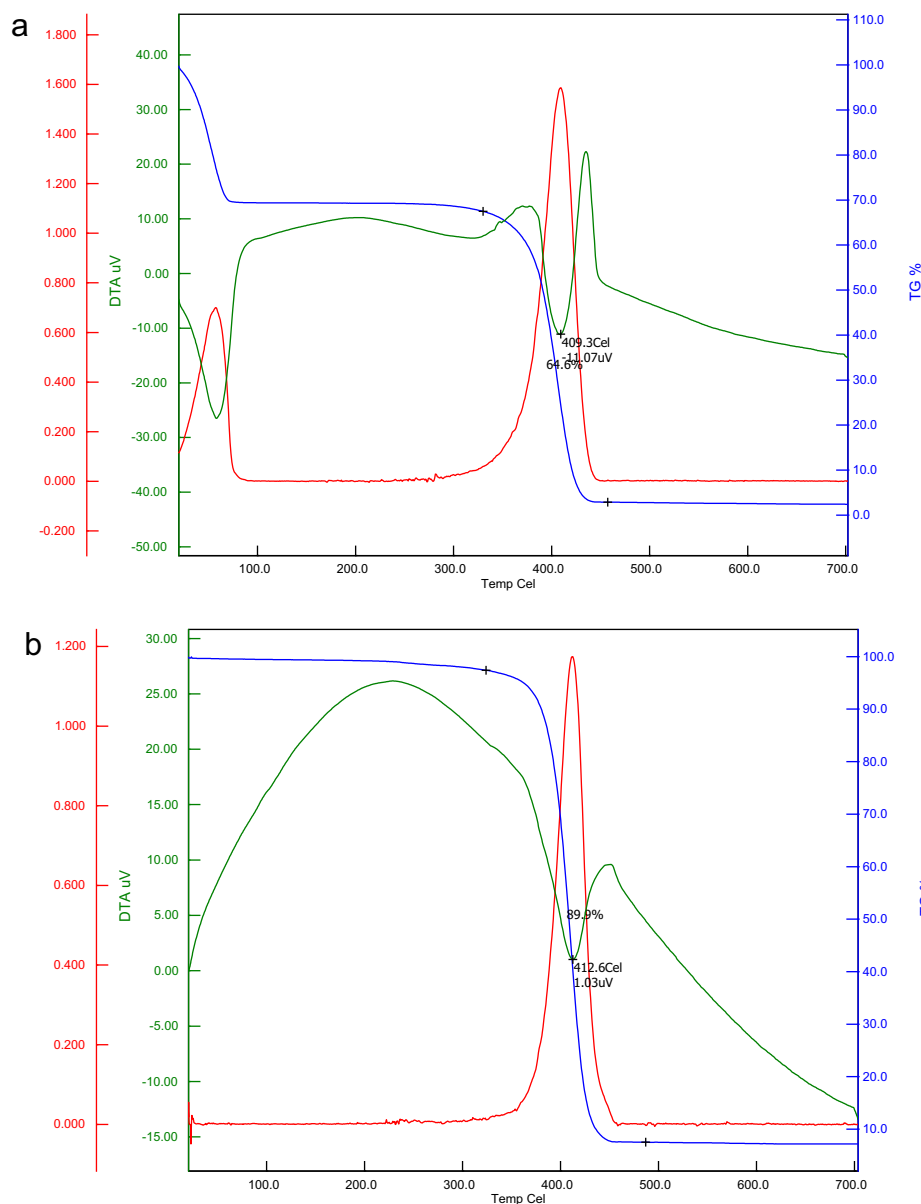


Fig. 1. Thermogravimetric and differential thermal analysis of (a) PS and (b)  $\text{TiO}_2$  immobilized PS before treatment.

photoactivity of produced catalyst were studied in the presence and absence of light. The solution pH was adjusted with 0.1 M NaOH or 0.1 M HCl solutions. A 15 mL portion of MB working solution and catalyst at certain concentration was placed in a quartz cell. Stock solution of MB ( $250 \text{ mg L}^{-1}$ ) was prepared and the solution was diluted to the working concentrations over the range  $15\text{--}105 \text{ mg L}^{-1}$ .

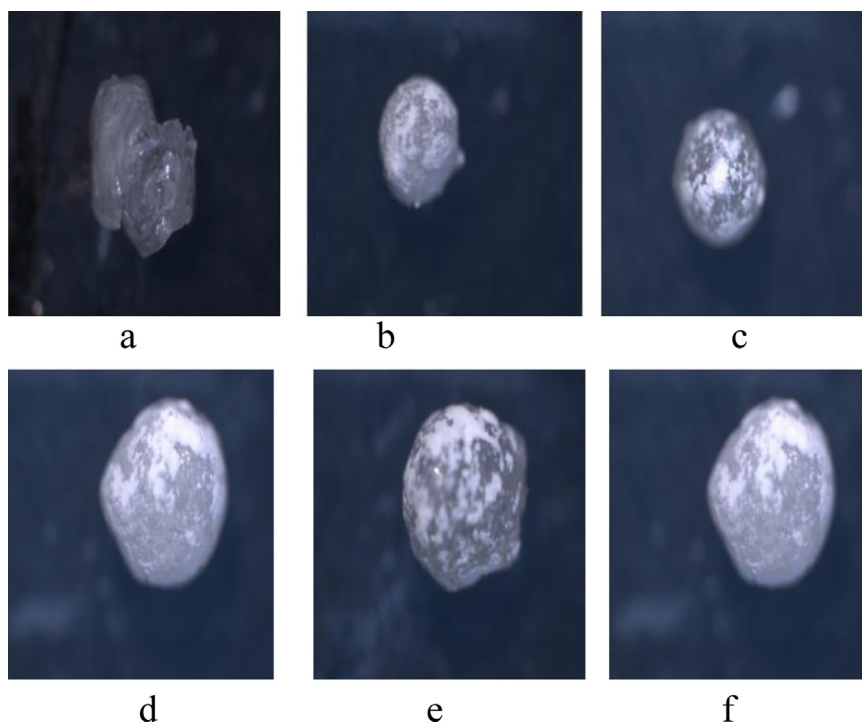
During the irradiation, the suspensions were sampled at regular intervals and centrifuged. The concentrations of the MB solutions were monitored by measuring their absorbance at 668 nm (Unicam UV-2 Spectrometer) over 150 min in the presence and absence of light. To determine the effect of the catalyst mass on the photocatalytic degradation of MB  $0.3\text{--}0.7 \text{ g}$  catalyst mass range was studied.

In the case of photo-reduction studies, a 30 mL solution of the desired Cr(VI) concentration was placed into the quartz cell and constantly stirred in the presence and absence of the light (365 nm). The photocatalytic activity was evaluated by the decrease in the Cr(VI) concentration. All photocatalytic reduction

experiments were performed at pH 2 since acidic pH had been previously proposed for more effective reduction of Cr(VI) to Cr(III) [30–32] and chromium ions present in its Cr(VI) state at this pH [33]. The initial pH of the working solution was adjusted by either  $\text{H}_3\text{PO}_4$  or NaOH. Stock solution of Cr(VI) ( $100 \text{ mg L}^{-1}$ ) was prepared in deionized water from  $\text{K}_2\text{Cr}_2\text{O}_7$ . The solution was diluted to the working concentrations over the range  $5\text{--}15 \text{ mg L}^{-1}$  Cr(VI).

To determine the effect of the catalyst mass on the photocatalytic reduction of Cr(VI)  $0.3\text{--}0.6 \text{ g}$  catalyst mass range was studied. Sacrificing agents are used to produce additional reductive electrons by occupying the positive holes ( $\text{h}^+$ ) formed during photocatalytic process so this enhance the photocatalytic reduction of Cr(VI) ions. Above experiments was also tested in the presence of hole scavengers such as ethylenediaminetetraacetic acid (EDTA), oxalic acid and methanol at  $15 \text{ mg L}^{-1}$  concentration (both Cr(VI) and sacrificing organic species).

The remaining chromium (VI) ions in the solution were monitored over a certain treatment period by photometric method at the 540 nm after colouring Cr(VI) with diphenylcarbazide [34].



**Fig. 2.** (a) Neat PS (b) TiO<sub>2</sub>-PS before treatment (c) TiO<sub>2</sub>-PS after treatment at pH 2 in water (d) at pH 7 in water (e) at pH 10 in water (f) in organic solvent ethanol.

Cr(VI)-diphenylcarbazide complex is formed at acidic medium. Triplicate runs were carried out for each test, and the standard deviations were calculated.

#### 2.4. Photokilling activity of TiO<sub>2</sub>-PS

*E. coli* (ATCC 25922), standard cultures were obtained from Karadeniz Technical University Medical School (Dept of Medical Microbiology, Trabzon) and cultured in Mueller-Hinton agarose (Merck, Germany). One day old cultures were placed into 3 mL strike Mueller-Hinton Broth (Merck, Germany) and it was incubated at 37 °C. The cells were re-suspended and diluted to  $1.5 \times 10^8$  CFU mL<sup>-1</sup> at 0.5 McFarland unite. This suspension was divided into 1 mL portions and stored at -80 °C until usage.

Prior to treatment the stock solution was defrosted and diluted in phosphate buffered saline (PBS, Medicago, Switzerland) to contain  $3 \times 10^4$  CFU mL<sup>-1</sup>. This solution was used for all experiments.

*A. niger* (DSM 1988) strain was grown in sabouraud 2% dextrose agarose and its spores were collected with distilled water. Spores were counted on Thoma lam to contain  $2 \times 10^6$  CFU mL<sup>-1</sup>. This suspension was divided into 1 mL portions and stored at room temperature. The working solution was prepared diluting 750  $\mu$ L of this suspension into 49.25 mL PBS. The number of cells of the solution was  $3 \times 10^4$  CFU mL<sup>-1</sup>.

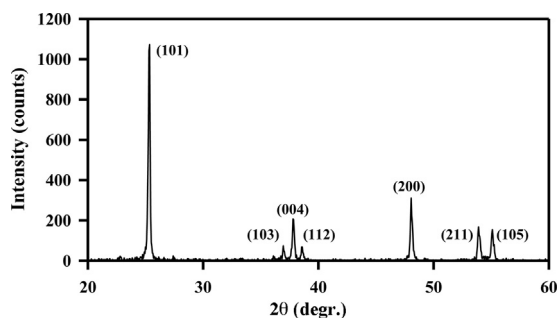
A 5 mL portion of this solution was placed in a quartz cell and 10  $\mu$ L portions were withdrawn at 10 min intervals during 60 min in the presence and absence of light and/or catalyst. The 10  $\mu$ L portions of *E. coli* or *A. niger* were directly cultivated on Mueller-Hinton agar or sabouraud dextrose agar plates, respectively. The plates were incubated for 24 h at 37 °C and the numbers of living colonies were counted to determine the number of viable cells expressed as the number of colony forming unit (CFU mL<sup>-1</sup>). The control experiments were necessary to confirm the condition of the bacterial and yeast, and act as a benchmark for the survival rate calculation. The method for testing the control sample was completely similar to TiO<sub>2</sub>-PS samples. Results were given as degradation percentage which was calculated from the number of colony

forming units before and after treatment of microorganisms. All experiments were carried out in triplicate to include the standard deviations. All equipments (Petri dishes, glassware and pipette tips) were sterilized by washing with ethanol and autoclaving at 170 °C for 1 h prior to usage.

### 3. Results and discussion

#### 3.1. Structural analysis of TiO<sub>2</sub>-PS

TGA analyses were carried out to determine the structural changes related to TiO<sub>2</sub> immobilization (Fig. 1). TGA analyses were repeated several times and average TiO<sub>2</sub> mass immobilized on PS was found to be  $3 \pm 0.1\%$  (w/w). The surface was also checked using binocular microscope before and after durability tests and TiO<sub>2</sub> particles were still seen on the surface after treatment in water at different pH (pH 2, 7 or 10) and in ethanol. It is evident that nanoparticles stable on the surface after treatment at different pH and organic solvent containing medium. XRD patterns verified that anatase TiO<sub>2</sub> nanoparticles were immobilized on PS surface (Fig. 3). SEM surface micrograph of TiO<sub>2</sub> immobilized PS is shown in Fig. 4(A) and



**Fig. 3.** The XRD pattern of the TiO<sub>2</sub>-PS.

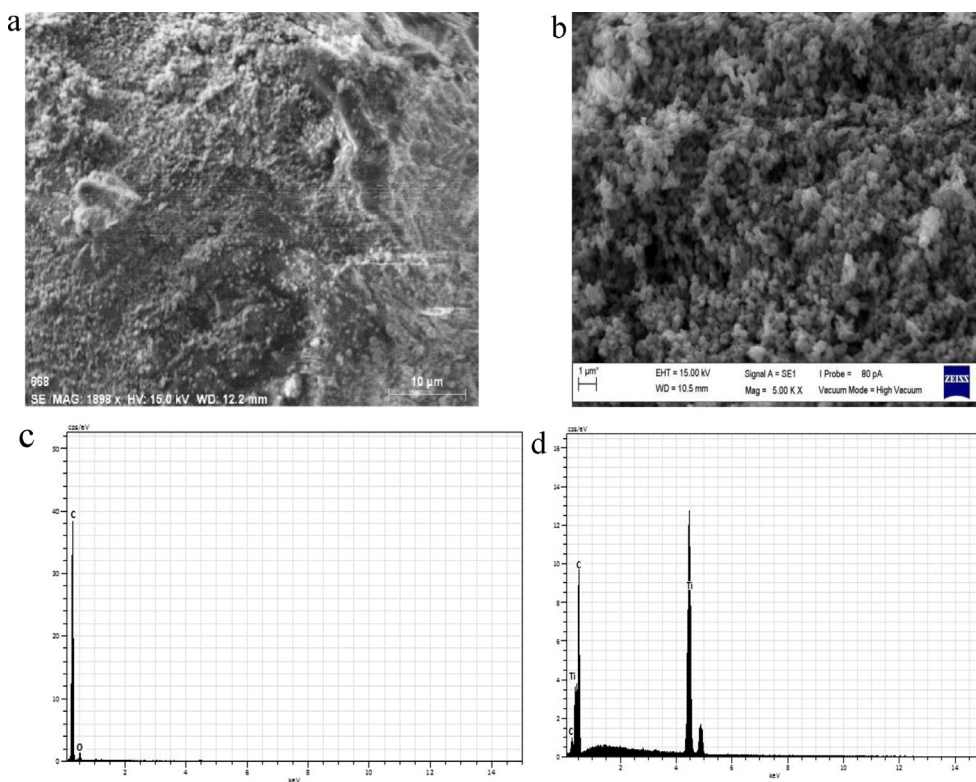


Fig. 4. The surface morphology of (a) neat PS and (b) TiO<sub>2</sub>-PS. The EDX analysis of (c) neat PS and (d) TiO<sub>2</sub>-PS.

(B). SEM images represent that the addition of TiO<sub>2</sub> on PS resulted in an uneven surface containing aggregated TiO<sub>2</sub> particles. Corresponding energy dispersive X-ray spectroscopy (EDX) indicated the presence of TiO<sub>2</sub> particles on the surface (Fig. 4(C) and (D)).

### 3.2. Photocatalytic degradation of MB and effects of reaction parameters

Photocatalytic removal of MB employing neat PS and TiO<sub>2</sub>-PS were monitored for 150 min (Fig. 5). As can be seen from the figure, total removal of 3 mg L<sup>-1</sup> MB solution has been achieved with TiO<sub>2</sub>-PS at quite high removal efficiency. Standard deviations were generally less than 1%.

The photodegradation of MB is influenced by a series of reaction parameters, such as pH, MB concentration and catalyst mass. These processes are usually more effective in acidic pH ranges and therefore the effect of the pH on the degradation of MB was

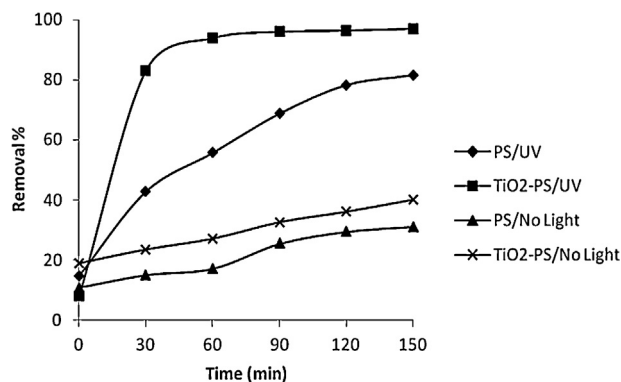


Fig. 5. The photocatalytic removal of MB ([MB] = 3 mg L<sup>-1</sup>, pH 6, catalyst mass = 0.1 g, V<sub>MB</sub> = 15 mL).

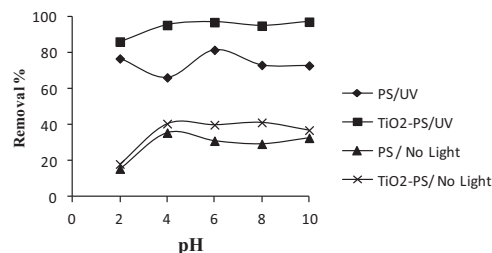


Fig. 6. The effect of pH on photocatalytic removal ([MB] = 3 mg L<sup>-1</sup>, catalyst mass = 6.66 g, V<sub>MB</sub> = 15 mL, 150 min irradiation time).

examined in pH range from 2 to 10 during 150 min treatment period (Fig. 6). The point of zero charge (pzc) of the TiO<sub>2</sub> photocatalyst (Degussa P25) is at pH 6.25 and TiO<sub>2</sub> surface is positively charged at lower pH (pH < 6.25), whereas it is negatively charged under alkaline conditions (pH > 6.25) [35]. Therefore, the efficiency of the MB removal is expected to increase by increasing pH because of the electrostatic interactions between the negative charged TiO<sub>2</sub> surface and the MB cations. As seen from Fig. 6 removal efficiency did not significantly change between 6 and 10. It is clear that MB

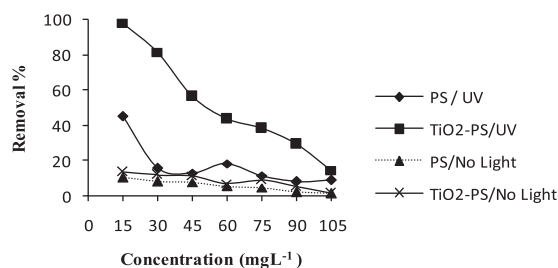
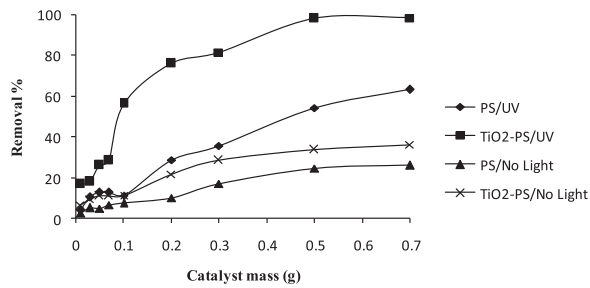
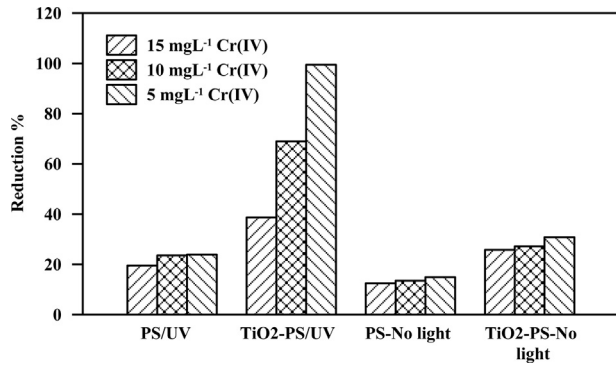


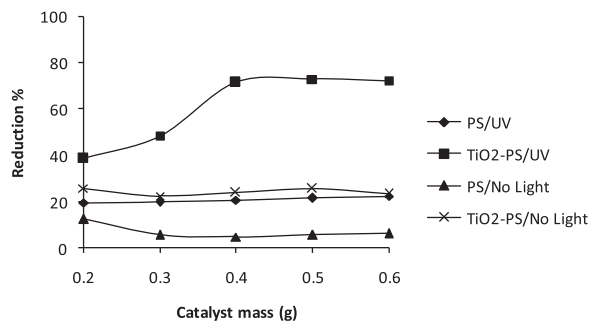
Fig. 7. The effect of initial concentration of MB on photocatalytic removal (pH 6, catalyst mass = 0.1 g V<sub>MB</sub> = 15 mL, 150 min irradiation time).



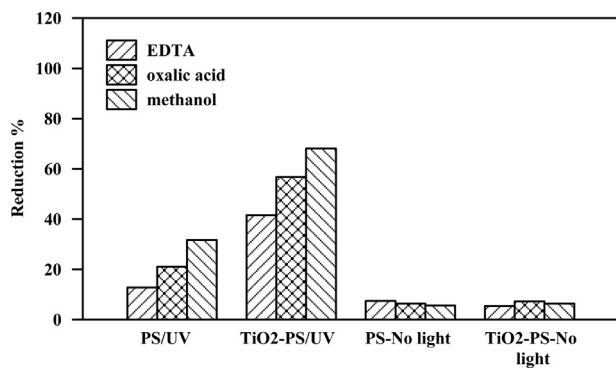
**Fig. 8.** The effect of catalyst mass on photocatalytic removal ( $[MB] = 45 \text{ mg L}^{-1}$ ,  $V_{MB} = 15 \text{ mL}$ , pH 6, 150 min irradiation time).



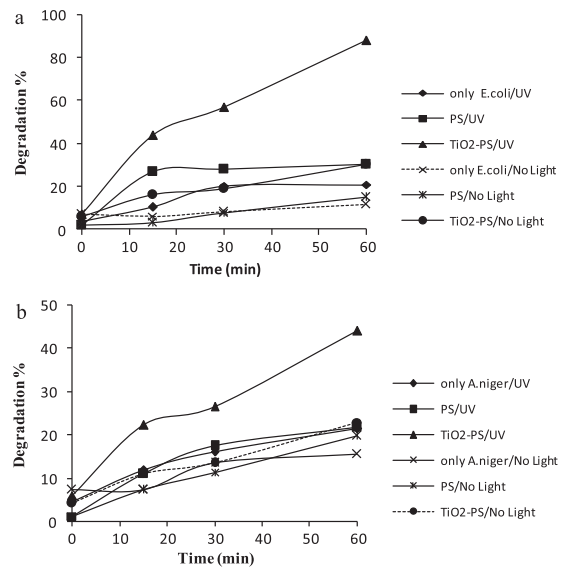
**Fig. 9.** The effect of initial concentration of Cr(VI) on photocatalytic reduction (pH 2, catalyst mass = 0.1 g,  $V_{Cr} = 15 \text{ mL}$ , 150 min irradiation time).



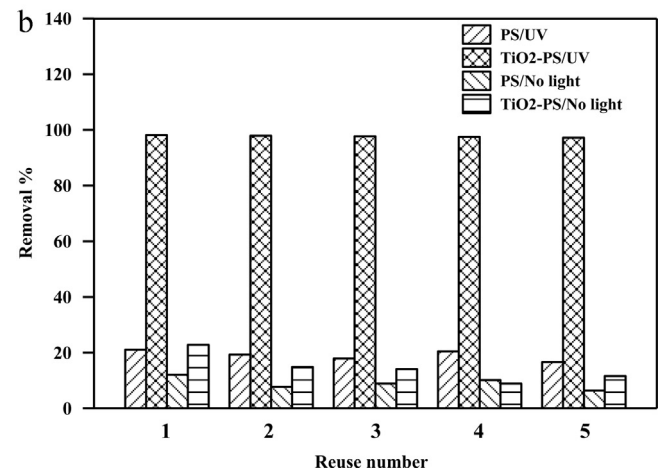
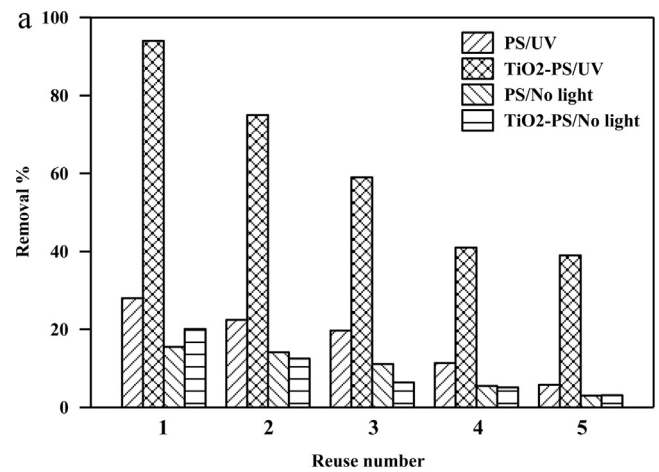
**Fig. 10.** The effect of initial catalyst mass on photocatalytic reduction of Cr(VI) ( $[Cr(VI)] = 15 \text{ mg L}^{-1}$ ,  $V_{Cr(VI)} = 15 \text{ mL}$ , pH 2, 150 min irradiation time).



**Fig. 11.** The effect of hole scavengers on the photocatalytic reduction of Cr(VI) ( $[Cr(VI)] = 15 \text{ mg L}^{-1}$ ,  $V_{Cr(VI)} = 15 \text{ mL}$ , [hole scavenger] =  $15 \text{ mg L}^{-1}$ , pH 2, 150 min irradiation time).



**Fig. 12.** Inactivation of (a) *E. coli* (b) *A. niger* in the presence and absence of light.



**Fig. 13.** Removal percentage of MB after 5 subsequent use ( $[MB] = 15 \text{ mg L}^{-1}$ , pH 6; catalyst mass = 0.1 g,  $V_{MB} = 15 \text{ mL}$ , 150 min.) (a) and Removal percentage of Cr(VI) after 5 subsequent use ( $[Cr(VI)] = 5 \text{ mg L}^{-1}$ ,  $V_{Cr(VI)} = 15 \text{ mL}$ , catalyst mass = 0.1 g, pH 2, 150 min) (b).

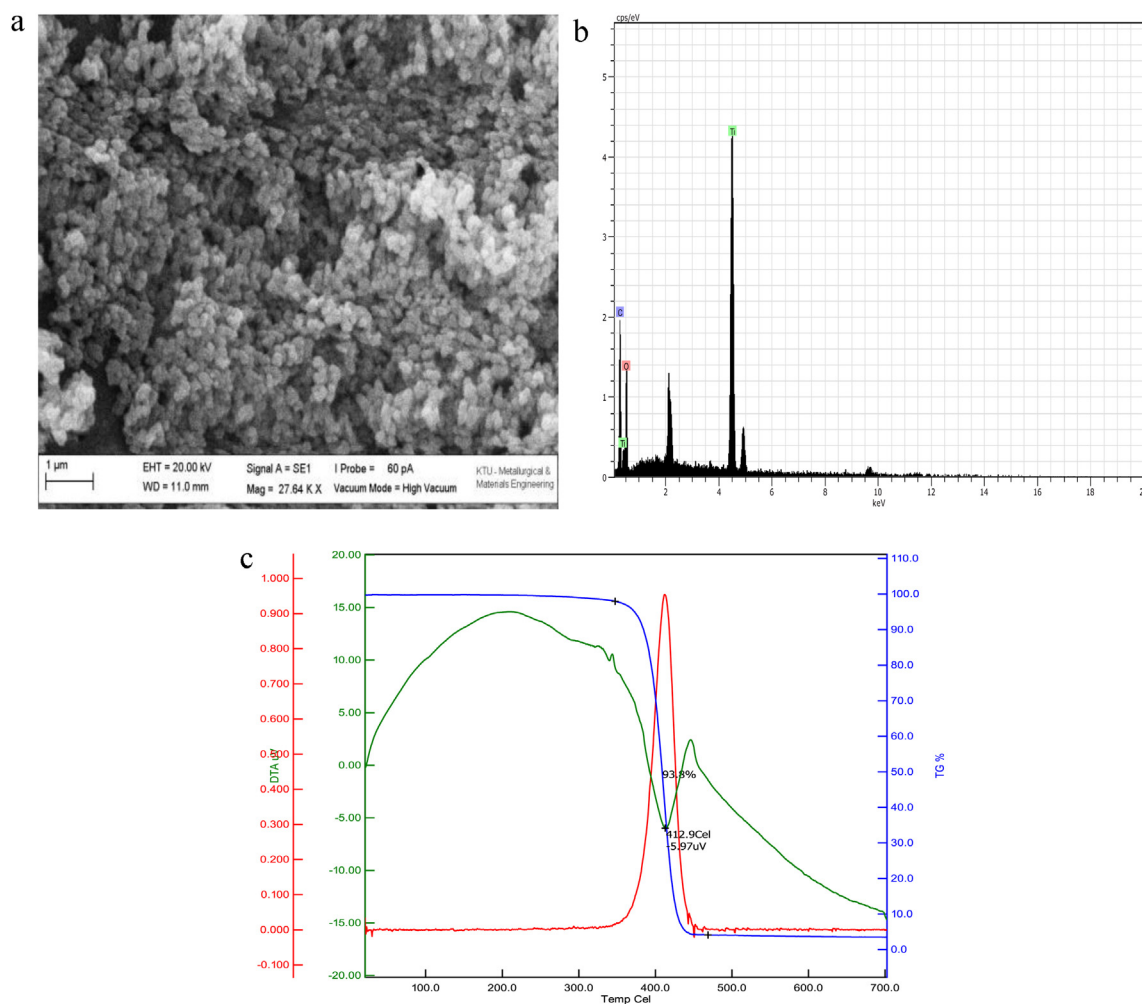


Fig. 14. SEM image (a), EDX (b) and TGA analysis (c) of TiO<sub>2</sub>-PS after 5 subsequent usage for photocatalytic treatment of MB.

was completely removed or degraded by TiO<sub>2</sub>-PS at its natural pH 6. This is an advantage since removal or degradation processes do not require additional pH arrangement.

In general, initial MB concentration is an important factor for the photocatalytic process. An increase in initial dye concentration of leads to an increase of photon path length and dye molecules can absorb more UV light than catalyst at higher concentrations [36]. As it is expected the photocatalytic removal of the MB decreased with increasing dye concentration (Fig. 7).

The effect of the catalyst mass on the MB photodegradation (Fig. 8) was also investigated. The amounts of dye molecules adsorbed on the surface increase with increasing catalyst. In conventional TiO<sub>2</sub> suspension system the higher catalyst mass increases the turbidity of the suspensions. In this case, the light penetration decreases, as a result of an enhanced light scattering effect, and consequently photocatalytic removal efficiency decreases [37]. However, turbidity problem has not been observed in our study since TiO<sub>2</sub> nanoparticles were immobilized on buoyant PS beads. As a result of this the percentage of photocatalytic removal increased as the amount of catalyst increases from 6.66 g L<sup>-1</sup> to 46.66 g L<sup>-1</sup>. It should be noted that higher MB concentration (45 mg L<sup>-1</sup>) was used for this test. A 100% removal was achieved by TiO<sub>2</sub>-PS at this concentration employing 46.66 g L<sup>-1</sup> catalyst without and turbidity problem.

### 3.3. Effects of the reaction parameters on the photocatalytic reduction of Cr(VI)

The produced TiO<sub>2</sub>-PS material was tested for photocatalytic reduction of Cr(VI) ions. The influence of initial metal concentration ranging from 5 mg L<sup>-1</sup> to 15 mg L<sup>-1</sup> on the photocatalytic reduction process was studied and results are given in Fig. 9. It can be seen from the figure that the photocatalytic removal percentages decreased with the increase in substrate concentration after 150 min illumination. However, removal rates showed no significant change in dark experiments. Photocatalytic removal percentages of 5 mg L<sup>-1</sup> Cr(VI) were significantly high reaching 100% after the same treatment period. Standard deviations were generally less than 1%.

The effect of catalyst mass on the photocatalytic reduction of Cr(VI) is also shown in Fig. 10. The removal increased with an increase in catalyst mass from 0.2 g to 0.3 g with and remained constant with no further increase observed on changes in catalyst mass.

One of the most important problems in photocatalytic processes is the undesired electron/hole recombination, which, in the absence of proper organic species, is highly efficient and leads to decrease of photocatalytic activity. One method to prevent electron-hole pair recombination is to add appropriate organic species as electron

acceptor or donor. They can inhibit recombination by increasing the number of trapped electrons, producing more radicals and enhance the reduction of Cr(VI). In this manner, we studied the effect of EDTA, oxalic acid and methanol on the photocatalytic reduction of chromium ions and the results obtained are shown in Fig. 11. The removal of Cr(VI) ions was greatly enhanced when the system contain both methanol or oxalic acid. These tests were carried out with high Cr(VI) initial concentration for better evaluation of sacrificing agents. Reduction percentage of  $15 \text{ mg L}^{-1}$  Cr(VI) after 150 min irradiation periods especially seem to be higher in the presence of methanol and follow the order: methanol (68.1%) > oxalic acid (56.7%) > EDTA (41.6%)

### 3.4. Photocatalytic disinfection of *E. coli* and *A. niger*

The efficacy of the  $\text{TiO}_2$  immobilized polystyrene against both microorganisms was monitored for 60 min under light exposure (Fig. 12). Control experiments employing PS or microorganisms alone in the presence and absence of light were also carried out under the same conditions. As can be seen from the results (Fig. 12(A)),  $\text{TiO}_2$ -PS was quite effective killing almost 89% of *E. coli* after 60 min exposure. However, only 30% of *E. coli* was killed in the presence of polystyrene and light alone.

It is clear that (Fig. 12(B)) *A. niger* seems to be much more resistant to the photocatalytic destruction than *E. coli* [38]. Standard deviations were generally less than 1%. The antibacterial effect of UV/ $\text{TiO}_2$  photocatalysis is due to the production of reactive oxygen species ( $\text{O}_2^{\bullet-}$ ,  $\text{H}_2\text{O}_2$  and  $\text{HO}^\bullet$ ) generated by actual light-activated  $\text{TiO}_2$ . These highly active species react with cell wall components and led to the lipid peroxidation, ultimately resulted in cell death. These mechanisms were previously discussed in details [39].

### 3.5. The photocatalytic reusability efficiency of $\text{TiO}_2$ -PS

The reusability tests of the  $\text{TiO}_2$ -PS were investigated for the MB and Cr(VI). After the first 150 min treatment the catalyst was simply washed with water and reused in a new treatment at the same pollutant concentration. The degradation or reduction percentages obtained after 5 times usage for MB or Cr(VI) are shown in Fig. 13. There is no significant decreased in photoreduction activity of  $\text{TiO}_2$ -PS for Cr(VI). However,  $\text{TiO}_2$ -PS activity decreased nearly 50% for MB removal after 5 cycles. It was clear that  $\text{TiO}_2$ -PS were still effective but dye removal rates were lower.

After photocatalytic treatment the surface of the materials were also re-checked. SEM images and EDX data of the films are given in Fig. 14. Surface morphology of  $\text{TiO}_2$ -PS were significantly unchanged or undamaged during the treatment process. However, after MB removal  $\text{TiO}_2$ -PS surface seemed to be occupied by dye molecules and it was slightly damaged in some areas. FT-IR and thermo gravimetric analyses revealed that polystyrene did not undergo any deformation after treatment. FT-IR spectrum (data were not given) and thermogram of  $\text{TiO}_2$ -PS were almost same before and after treatment.

## 4. Conclusion

In this study, a very simple technique has been presented to prepare  $\text{TiO}_2$  catalyst immobilized on polystyrene material by thermal attachment method. The produced materials successfully removed MB and Cr(VI) from aqueous solution under ambient

conditions. The optimization of various reaction parameters produced significant increase in the removal efficiency. The addition of organic additives especially methanol enhanced the Cr(VI) reduction process. Spectroscopic and structural analyses revealed that  $\text{TiO}_2$  immobilized PS was resistant to structural changes and can be re-used until a significant decrease in the photocatalytic efficiency.  $\text{TiO}_2$  immobilized onto PS provided high kill-rates for *E. coli* and *A. niger* in shorter time (60 min). This research is useful for the preparation of highly active photocatalytic material under more environmentally favourable conditions. The produced material can be used for several environmental applications, since its excellent floating properties do not require sophisticated filtration techniques to separate the nanoparticles. Additionally,  $\text{TiO}_2$ -PS has excellent properties due to its polystyrene content in combination with antimicrobial action. It can be used in construction industry as joint sealant. Usability of the material will be tested for these properties in the future.

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